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⑤④ **Adhesive containing microcapsules.**

⑤⑦ A microcapsule type adhesive for preventing the loosening of screw and the like, superior in storage stability, adhesive force and safety, is provided.
The microcapsule type adhesive comprises an epoxy resin as a core material and an aldehyde resin or urea resin as a wall material, a water-soluble polyacetal resin binder, and a non-volatile, water-soluble or water-dispersible amine-based curing agent.

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Background of the Invention

The present invention relates to a microcapsule type adhesive to be applied to a threaded surface of a threaded member such as screw, bolt, nut, or the like, to prevent loosening or to impart a close-contact property (both hereinafter referred to as "prevent loosening") thereto.

Heretofore, as a loosening preventing adhesive to be applied to a threaded surface (screw thread) of a threaded member such as screw, bolt, nut, or the like, there has been known a composition comprising a microcapsule containing a reactive adhesive and a resin as a binder, using an organic solvent or water as a solvent, for example in Japanese Patent Publication Nos. 11051/1970 and 46339/1977 and Japanese Patent Laid Open Nos. 308876/1990 and 11883/1978.

However, such known microcapsule type adhesives have certain drawbacks such as poor adhesion, poor storage stability and likelihood of causing environmental pollution. For example, if an emulsion such as an acryl emulsion, is used as a binder, or a dispersion type binder is used, the emulsifying or dispersion stability is impaired by the curing agent used, resulting in increased viscosity and difficulty of application in many cases. And in the case where polyvinyl alcohol or gelatin film is used as a wall film, it is difficult to prevent the deterioration of its performance due to swelling caused by water for example. Moreover, the use of an acrylic resin as a reactive adhesive causes deterioration not only in bonding strength at high temperatures but also in solvent resistance. Further, many conventional microcapsule type adhesives employ organic solvents, but the use of organic solvents not only causes the problem of environmental pollution but also may badly affect the worker's health during application to screw, bolt, nut, or the like.

It is the object of the present invention to solve the above-mentioned problems of the prior art.

Summary of the Invention

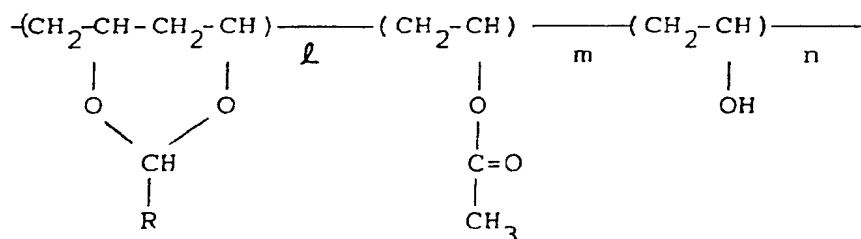
According to the present invention there is provided a microcapsule type adhesive for preventing the loosening of screw, bolt, nut, or the like, characterized by comprising (A) a microcapsule using a curable epoxy resin as a core material and an aldehyde resin or urea resin as a wall material, (B) a water-soluble polyacetal resin binder and (C) a non-volatile water-soluble or -dispersible amine-based curing agent.

As the curable epoxy resin which constitutes the core of the microcapsule in the present invention there is used a conventional water-insoluble epoxy resin having an epoxy group in the molecule. A preferred example is one having a viscosity of not higher than 100,000 mPa·s and which is easily encapsulated. As examples of such epoxy resin there are mentioned reaction products of polyhydric alcohols such as bisphenol A and epichlorohydrin, polyglycidyl ether and epichlorohydrin, phenolformaldehyde condensation polymer and epichlorohydrin, aminephenol and 1,2-epoxy resin.

As the wall material of the microcapsule in the invention there is used an aldehyde resin or a urea resin. As examples of the aldehyde resin are mentioned conventional ones such as urea-formaldehyde resin and melamine-formaldehyde resin. Examples of the urea resin include polyureas and polyurethanes. The wall film does not exhibit a swelling property for water and is impermeable to water.

It is the essence of the present invention to use a water-soluble polyacetal in combination with the microcapsule of the above construction.

A preferred example of such water-soluble polyacetal is one obtained by acetalizing a partial hydrolyzate of polyvinyl acetate with an aldehyde. Typical examples thereof are those represented by the following formula:



where $\ell=1\sim 15$, $m+n=85\sim 99$, and R is an alkyl group having 1 to 4 carbon atoms.

As to the curing agent used in the invention, it is necessary to select one which can cure the epoxy resin contained in the microcapsule quickly at room temperature collapse of the microcapsule and contact of the curing agent with the epoxy resin therein and which does not volatilize in an applied state to a screw or the like. As the curing agent, a water-soluble or -dispersible amine-based curing agent which is non-volatile at

room temperature, is used in the present invention.

As examples of the curing agent are mentioned amines in a narrow sense such as imidazole, 1,3-bis-4-piperidylpropane, 1,6-hexadiazine, methylenedianiline, substituted alkylendiamine, and liquid polyamides, e.g. Versamid 125 (a dimerized saturated aliphatic acid reacted with alkylendiamine), as well as amine adducts such as non-volatile solid amine salts prepared by the reaction of volatile liquid amines and acids, and water-soluble polyamide resins.

The ingredients of the microcapsule type adhesive of the present invention are preferably in the proportions of 10-60 parts by weight of the microcapsule, 5-35 parts by weight of the binder, 5-30 parts by weight of the curing agent and 10-80 parts of water.

In the state of a liquid composition before application of the microcapsule type adhesive of the present invention, changes in quality such as swelling of the capsule and curing the internal adhesive ingredients through the capsule are suppressed and thus the adhesive possesses a superior storage stability. Besides, the combination of the capsule with the water-soluble polyacetal resin binder permits the capsule to be fixed to a threaded surface efficiently with an excellent adhesive force.

Moreover, a high bonding strength in a hot condition and a high bonding force in a normal state can be attained by a synergistic effect of those ingredients and the epoxy resin and amine-based curing agent. Since the use of an organic solvent is not required in the present invention, there is further attained an advantage that there is no risk of environmental pollution or bad influence on the worker's health.

[Examples]

Adhesive compositions were prepared in such compositions as shown in Tables 1 and 3 below, then each applied to a bolt (diameter: $M = 10$ mm) and air-dried to prepare test pieces.

Torque Test: The test pieces were tightened at 300 kg-f-cm, then allowed to stand for 3, 5, 10, 24 and 48 hours, and thereafter untightening torques were measured.

Storage Stability Test: The adhesive compositions were subjected to a storage promotion test at 40°C for 30 days. After tightening in the same manner as in the above torque test, the test pieces with the thus-stored adhesive compositions were allowed to stand for 24 hours, and thereafter untightening torque were measured.

The water-soluble polyacetal used was prepared by partially acetalizing a partial hydrolyzate of vinyl acetate with aldehyde. (In the following tables, the value of R represents the number of carbon atom.). the results obtained are as set forth in Table 2 and 4.

Table 1

	Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3
Epoxy capsule (Wall film: urea formaline)	20	20	20	
Epoxy capsule (Wall film: gelatin)				20
Water-soluble polyacetal ($\ell=5$, $m=15$, $n=80$, $R=4$)	3			3
Acryl emulsion		3		
Polyvinyl alcohol			3	
Silica powder	5	5	5	5
Pure water	8	8	8	8
1,3-Dipiperidylpropane	14	14	14	14

(Part by weight)

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Table 2

Item	Torque (kg·f·cm)			
	Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3
<u>Torque Test</u>				
after 3 hrs	220	-	-	-
after 5 hrs	280	-	-	-
after 10 hrs	350	-	-	-
after 24 hrs	495	390	-	546
after 48 hrs	540	385	-	550
<u>Storage Stability Test</u>				
after 24 hrs	480	370	-	-
Remarks		1*	2*	3*

1* Tightening caused drop-out of capsule.

2* Viscosity increased to an unapplicable extent during mixing.

3* Composition increased in viscosity in 3 to 4 hours.

TABLE 3

	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Epoxy capsule (wall film: urea-urethane)	10	5	6	
Epoxy capsule (wall film: polyurethane)				10

Table 3

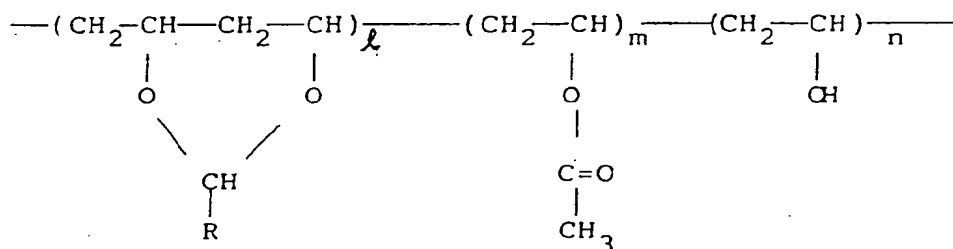
	Ex. 2	Ex. 3	Ex. 4	Ex. 5
<u>Water-soluble polyacetal</u> ($l=10$, $m=10$, $n=80$, $R=2$)	5			
<u>Water-soluble polyacetal</u> ($l=15$, $m=3$, $n=82$, $R=1$)		15	1	5
Silica powder	3			3
Pure water	25	26	40	25
1,3-Dipiperidylpropane	7	4		
Water-soluble amine (AHA-23, a product of ACR, Co.)			3	
Water-soluble amine (H-4121, a product of ACR, Co.)				7

Table 4

Item	Torque (kg·f·cm)			
	Ex. 2	Ex. 3	Ex. 4	Ex. 5
<u>Torque Test</u>				
after 3 hrs	440	215	200	410
after 5 hrs	450	290	220	460
after 10 hrs	550	320	220	460
after 24 hrs	630	320	240	500
after 48 hrs	600	335	300	600
<u>Storage Stability Test</u>	640	290	200	600

Claims

1. A microcapsule type adhesive for preventing the loosening of a threaded member, comprising: (A) a microcapsule using an epoxy resin as a core material and an aldehyde resin or urea resin as a wall material; (B) a water-soluble polyacetal resin binder; and (C) a non-volatile, water-soluble or water-dispersible amine-based curing agent.
2. A microcapsule type according to claim 1, wherein the water-soluble polyacetal resin is represented by the following formula:



where $\ell=1\sim 15$, $m+n=85\sim 99$, and R is an alkyl group having 1 to 4 carbon atoms.

3. A microcapsule type adhesive according to claim 1 or claim 2 comprising 10-60 parts by weight microcapsule, 5-35 parts by weight binder, 5-30 parts by weight curing agent and 10-80 parts by weight water.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 31 0649

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 063 475 (CAPSULATED SYSTEMS INC.) * page 3, line 14 - line 24; claims 1,6 * ---	1	C09J129/14 C09J163/00
A	FR-A-1 587 880 (MINNESOTA MINING AND MANUFACTURING CORP) * claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C09J C08G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 FEBRUARY 1993	Examiner Dieter Schüler
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